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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08G 18/42		A1	(11) International Publication Number: WO 97/30100
			(43) International Publication Date: 21 August 1997 (21.08.97)
(21) International Application Number: PCT/US97/02113		O'BRIEN, Michael, E. [US/US]; 208 E. Littleton Trail, Hainesville, IL 60030 (US). HILLSHAFFER, Douglas, Kip [US/US]; 4224 Clausen, Western Springs, IL 60558 (US). (74) Agent: SARUSSI, Steven, J.; McDonnell Boehnen Hulbert & Berghoff, 300 South Wacker Drive, Chicago, IL 60606 (US). (81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 13 February 1997 (13.02.97)			
(30) Priority Data: 60/011,649 14 February 1996 (14.02.96) US 60/029,730 23 October 1996 (23.10.96) US 60/029,597 28 October 1996 (28.10.96) US			
(60) Parent Applications or Grants (63) Related by Continuation US 60/029,730 (CIP) Filed on 23 October 1996 (23.10.96) US 60/029,597 (CIP) Filed on 28 October 1996 (28.10.96) US 60/011,649 (CIP) Filed on 14 February 1996 (14.02.96)			
(71) Applicant (for all designated States except US): STEPAN COMPANY [US/US]; 22 West Frontage Road, Northfield, IL 60093 (US).			
(72) Inventors; and (75) Inventors/Applicants (for US only): FAUNCE, James, A. [US/US]; 705 Pinhurst, North Aurora, IL 60542 (US).		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: PHTHALIC ANHYDRIDE BASED POLYESTER POLYOLS FOR IMPROVED HYDROLYTIC STABILITY IN URETHANE-BASED COATINGS, ADHESIVES, SEALANTS AND ELASTOMERS			
(57) Abstract Disclosed are methods for imparting improved hydrolytic stability to a coating, adhesive, elastomer and/or sealant (CASE). The methods involve the addition of a phthalic anhydride derived polyester polyol. Also disclosed are non-foam hydrolytically stable urethane and pre-urethane compositions useful in the preparation of CASE materials, with improved hydrolytic stability.			

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PHTHALIC ANHYDRIDE BASED POLYESTER POLYOLS FOR IMPROVED HYDROLYTIC STABILITY IN URETHANE-BASED COATINGS, ADHESIVES, SEALANTS AND ELASTOMERS

5

BACKGROUND OF THE INVENTION

Field of the Invention

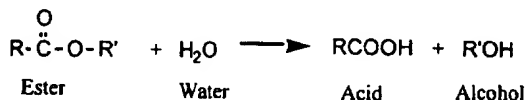
This invention relates to hydrolytically stable, non-foam urethane compositions such as coatings, adhesives, sealants, and elastomers containing phthalic anhydride-based polyester polyols and methods imparting improved hydrolytic stability to non-foam urethane coatings, adhesives, sealants, elastomers and the like.

Description of the Related Art

Desirable physical properties of polyurethane coatings, adhesives, sealants and elastomers (CASE) include, among others, durability, flexibility, rigidity, hardness, toughness, resistance to abrasion, ability to bond to various substrates, and resistance to chemicals; one of the most desirable properties is hydrolytic stability. Coatings, adhesives, sealants and elastomers which are not resistant to hydrolysis undergo chain scission and gradual degradation of the other physical properties. Industrial polyurethanes are generally made from the reaction of polyisocyanates and materials with multiple hydroxyl moieties ("polyols"). In many adhesive and coatings formulations, polyols comprise the majority of the formulation weight, so that the final product properties are influenced mostly by the polyols.

Of the commercially available polyols, polyether- and polyester-containing materials are dominant. Polyether polyols are usually based on propylene oxide, ethylene oxide or tetrahydrofuran. These typically exhibit very good resistance to hydrolysis, which is an important requirement of many adhesives and coatings. However, polyether polyols promote adhesion to a very limited variety of substrates. In contrast, polyester polyols generally

promote adhesion to more types of surfaces but are more susceptible to hydrolysis. Typically, a polyester molecule is hydrolyzed to an acid and alcohol as shown below. The hydrolysis may be acid or base catalyzed.



- 5 The deleterious consequence of such hydrolysis in a polyurethane material is the loss of desirable physical properties, as hydrolysis gives undesirable products with lower molecular weight.

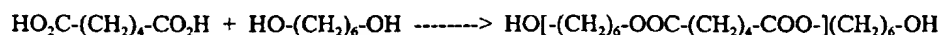
In addition, polyester polyols are utilized in non-foam formulations to improve physical properties such as toughness, tensile and flexural strength, durometer hardness, solvent resistance, and thermal properties. Urethane coatings, and other applications, based on polypropylene oxide polyols and toluene diisocyanate have found limited applications, i.e. indoors only, as also they contain contaminant ether linkages which are readily prone to oxidative degradation. CASE materials derived from polyester polyols, such as those prepared by the condensation of an aliphatic dicarboxylic acids and poly alcohols, are widely used indoors and outdoors. Their primary function in finished CASE materials has been to enhance abrasion resistance. While these CASE materials possess better durability than those based on polypropylene oxide polyols and toluene diisocyanate, they also contain ether groups that undergo oxidative degradation.

Aliphatic polyester polyols, which contain ether linkages and/or ester linkages have found wide spread use in CASE, as additives which can provide improved bonding and durability. These materials are generally based on caprolactone or adipic acid backbones. One of the more widely used commercial polyester polyols is based on polycaprolactone and sold under the trade name Tone® (Union Carbide Corp.). This polyester polyol is the product of

the homopolymerization of caprolactone with a hydroxyl containing compound as an initiator, such as a diol, to form polycaprolactone polyols.

These polyester polyol materials are highly compatible, hydrolytically stable, resistant to yellowing, display excellent abrasion, chemical and impact resistance, they provide
5 excellent resistance to oxidative degradation, and are considered to be the leaders in the commercial products which are currently available. The greatest drawback to the use of these materials is their very high manufacturing cost, a drawback which is very unfavorable from a consumer point-of-view.

Aliphatic polyester polyols based on adipic acid are prepared by the condensation of
10 adipic acid and a diol, such as 1,6-hexanediol, as shown below:



These materials are well known to undergo hydrolytic degradation at the ester linkage sites of
15 the molecule. However, the materials have the advantage of a low manufacturing cost, as compared to Tone® type materials, which is favorable from a consumer point of view.

Polyester polyols derived from phthalic anhydride (PA) and low molecular weight diols are reported in U.S. 4,644,027 to Magnus et al., issued Feb. 17 1987 and U.S. 4,644,047 to Wood, issued Feb. 17, 1987, for the production of cellular polyurethane and
20 polyurethane/polyisocyanurates. Polyester polyols derived from PA and neopentyl glycol have been reported in U.S. 4,390,688 to Walz et al., issued Jun. 28, 1983. These materials are described as water dilutable polyesters with good resistance to xylene and dilute caustic solutions. PA polyester polyols have been used in polyurethane/ polyisocyanurate rigid foams to impart low thermal conductivity, to lower cost and to lower blowing agent usage as
25 reported in U.S. 4,791,148 to Riley et al., issued Dec. 13, 1988; U.S. 4,888, 365 to Riley et al., issued Dec 19, 1989 and U.S. 5,164,422 to Londrigan et al., issued Nov. 17, 1992. The

PA based polyester polyols have been used in the preparation of urethane-modified isocyanurate foam as reported in U.S. 4,544,679 to Tideswell et al., issued Oct. 1, 1985.

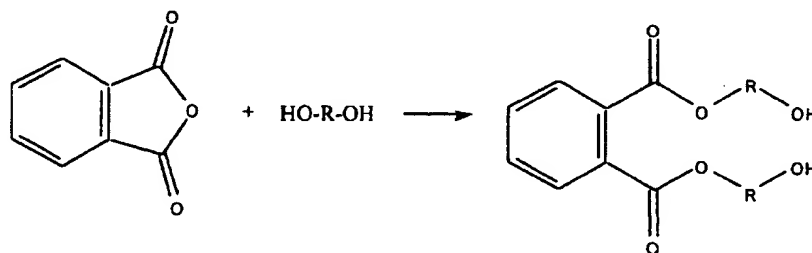
Rigid foams have incorporated PA-based polyester polyols and perfluorinated hydrocarbons to enhance the thermal insulating properties of the foam, as reported in U.S.
5 4,981,879 to Snider, issued Jan. 1, 1991 and EP 394736 A2, Snider et al., Oct. 31, 1990.

SUMMARY OF THE INVENTION

This invention relates to the use of phthalic anhydride based polyester polyols in coating, adhesive, sealants and elastomers for improved hydrolytic stability. It has been surprisingly discovered that phthalic anhydride based polyester polyols are more stable to hydrolysis and provide improved overall hydrolytic stability to non-foam urethanes such as coating, adhesive, sealant and elastomer formulations, as compared to non-phthalic anhydride based polyester polyols of similar molecular weights, such as caprolactone based polyester polyols, adipic acid based polyester polyols, terephthalate based polyester polyols, isophthalate based polyester polyols, and other aliphatic based polyester polyols. The phthalic anhydride based polyester polyols provide a unique combination of improved hydrolytic stability and improved adhesion properties which allow for formulation simplification.

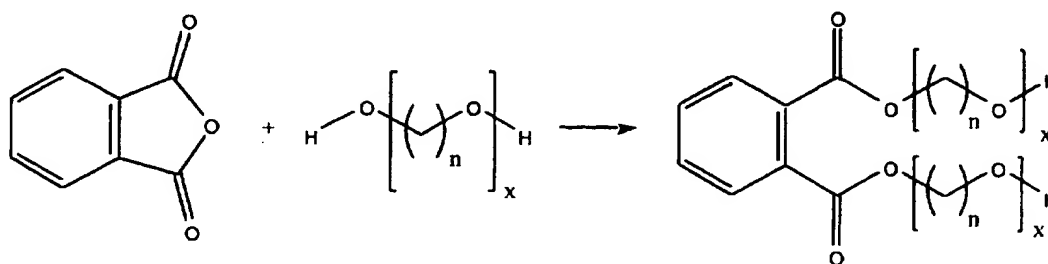
It has been discovered that aromatic polyester polyols which contain two ester functionalities on an aromatic ring, wherein one ester linkage is located at a position *ortho* to that of the other ester linkage on the aromatic ring, are unexpectedly more resistant to hydrolysis, as compared to polyester polyols wherein one ester linkage is located at a position *meta* or *para* to that of the other ester linkage. These polyester polyols show a diminished increase in acid number (which is correlated to hydrolysis) at elevated temperature and various moisture concentrations, as compared to other commercially available aromatic- and aliphatic-ester polyols of similar equivalent molecular weight.

The polyester polyols of the present invention are derived from the reaction of phthalic anhydride (PA) and a polyhydroxyl compound as shown below:



wherein R is branched or linear alkyl, cycloalkyl, alkenyl, alkynyl, aromatic, polyoxyethylenic, polyoxypropylenic; wherein R may contain pendant secondary functionality such as aldehyde, ketone, ether, ester, amide, nitrile, amine, nitro, thiol, sulfonate, sulfate, and/or carboxylic groups.

- 5 While a wide variety of polyhydric alcohols may be utilized in the present invention, preferred PA polyester polyols are of the form



- wherein $n = 2-10$, $x = 1-500$. Highly preferred PA polyester polyols for use in the present invention are derived from the condensation of phthalic anhydride and ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, neopentyl glycol, 1,4-butanediol, 1,6-hexanediol, polyethylene glycol and polypropylene glycol.
- 10

The phthalic anhydride based polyester polyols are compatible with atmospheric curing, heat curing, and exhibit normal pigmentation compatibility.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph of acid number in mg KOH/g (plotted on the vertical (Y) axis) vs. time in hours for Tone®, spiked with benzoic acid (filled squares), adipic acid (open squares) or the half-ester (HAE) of phthalic anhydride (filled diamonds).

5 Figure 2 is a graph of acid number in mg KOH/g (plotted on the vertical (Y) axis) vs. time in hours for various polyols obtained during a hydrolysis study. Filled squares represent Sample A, STEPANPOL® PS-2002; open squares represent Sample B, Tone®; and filled diamonds represent Sample C, Fomrez®.

10 Figure 3 is a graph of acid value in mg KOH/g vs. time in hours for hydrolysis of polyester polyols with 10% water at 200°F. Filled diamonds represent hydrolysis of a caprolactone based polyester polyol; and filled squares represent hydrolysis of STEPANPOL® PS-2002, a phthalic anhydride diethylene glycol polyester polyol.

15 Figure 4 is a graph of acid value in mg KOH/g vs. time in hours for hydrolysis of polyester polyols (all diethylene glycol based) with 10% water. Filled diamonds represent hydrolysis of an terephthalic acid based polyester polyol; filled triangles represent hydrolysis of STEPANPOL® PS-2002, a phthalic anhydride based polyester polyol; and filled squares represent hydrolysis of a isophthalic acid based polyester polyol.

DETAILED DESCRIPTION OF THE INVENTION

The invention encompasses a method for preparing a hydrolytically stable, non-foam urethane coating, adhesive, sealant and/or elastomer, the improvement comprising the adding of an amount sufficient to impart hydrolytic stability to the non-foam urethane coating, adhesive, sealant and/or elastomer of a phthalic anhydride-derived or phthalic acid-derived polyester polyol.

The invention encompasses methods for preparing a hydrolytically stable, non-foam urethane coating, adhesive, sealant and/or elastomer utilizing compositions suitable for preparing non-foam urethane coatings, adhesives, elastomers or sealants, wherein the compositions comprise

(a) from about 10 % to about 60% based on the weight of the composition of a polyisocyanate;

(b) from about 0.02 % to about 5.0 % based on the weight of the composition of a urethane catalyst; and

(c) from about 10% to about 90% based on the weight of the composition of a high aromatic, low acid number phthalate polyester polyol blend comprising:

(1) from about 2 - 60 weight percent of a phthalic acid material selected from the group consisting of phthalic anhydride or phthalic acid; and

(2) from about 40 - 98 weight percent of at least one polyol of the formula:

HO-R₁-OH

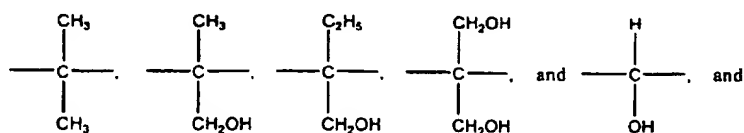
wherein R₁ is a divalent radical selected from the group consisting of:

(a) alkylene radicals of about 2 to 10 carbon atoms;

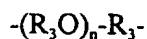
(b) radicals of the formula:

-CH₂-R₂-CH₂-

where R₂ is a radical selected from the group consisting of:



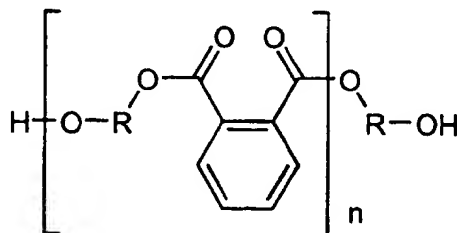
(c) radicals of the formula:



where R_3 is an alkylene radical containing from about 2 to about 4 carbon atoms, and n is an integer of from about 0.1-200.

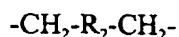
In a more preferred embodiment the phthalate polyester polyol blend comprises from about 20 - 60 weight percent of a phthalic acid material selected from the group consisting of phthalic anhydride or phthalic acid and from about 40 - 80 weight percent of at least one polyol. Compositions of the present invention are substantially free of CFC and/or hydrocarbon blowing agents (i.e. they contain less than 1% by weight of a blowing agent) and are thus, generally not intended to be used in open or closed celled foam applications. The resulting urethane compositions are free or substantially free from open-cell or closed-cell cellular structure, i.e., they are not foams. Preferred compositions for preparing the urethanes of the invention contain from about 50-90% by weight of the composition of the phthalic anhydride based polyester polyol. Most preferred compositions for preparing the urethanes of the invention contain from about 60-80% by weight of the composition of the phthalic anhydride based polyester polyol. Optionally, compositions of the present invention may additionally contain from about 0.01 - 20.0 % by weight of a polyisocyanurate.

A preferred polyester polyol for use in the invention has the formula:

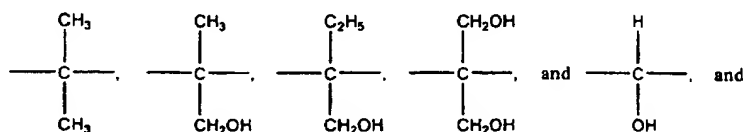


wherein R is a divalent radical selected from the group consisting of:

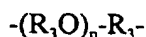
- (a) alkylene radicals of about 2 to 10 carbon atoms;
- (b) radicals of the formula:



5 where R_2 is a radical selected from the group consisting of:



- (c) radicals of the formula:



where R_3 is an alkylene radical containing from about 2 to about 4

10 carbon atoms, and n is an integer of from about 0.1 - 200.

Specific polyester polyols suitable for use in the methods and compositions of the invention include phthalic acid diethylene glycol polyester polyols. Suitable phthalic acid diethylene glycol polyester polyols are commercially available from Stepan Company, Northfield, Illinois. Representative polyols are StepanPol® PS-2002 (a phthalic anhydride
15 diethylene glycol polyester polyol having an OHv of 200 and a functionality of 2), StepanPol® PS-3152 (a phthalic anhydride diethylene glycol polyester polyol having an OHv of 315 and a functionality of 2), and StepanPol® PS-4002 (a phthalic anhydride diethylene glycol polyester polyol having an OHv of 400 and a functionality of 2), and mixtures thereof.

20 By OH value (OHv) is meant hydroxyl value, a quantitative measure of the concentration of hydroxyl groups, usually stated as mg KOH/g, i.e., the number of milligrams of potassium hydroxide equivalent to the hydroxyl groups in 1 g of substance.

By functionality is meant the number of reactive groups, e.g., hydroxyl groups, in a chemical molecule.

Although not critical to the present invention, the compositions of the present invention may optionally contain from about 0.01 - 50.0 percent by weight of a cross linking agent. Suitable cross linking agents are, for example, higher functionality alcohols such as triols or pentaerythritol.

5 A wide variety of urethane catalyst are suitable for use in the present invention. Generally, any urethane catalyst capable of effecting a polymerization to form a urethane CASE may be used in the present invention. Examples of suitable urethane catalysts include, among others, tetramethylbutanediamine (TMBDA), 1,4-diaza(2,2,2)bicyclooctane (DABCO), dibutyltindilaurate (DBTDL) and tinocatoate (SnOct), and mixtures thereof.

10 Although somewhat less desirable, the compositions of the present invention may optionally contain from about 0.01 - 50.0 percent by weight of a polyether-based polyol. Examples of suitable polyether-based polyols include, among others, the condensation products of propylene glycol/propylene oxide, trimethylolpropane/ethylene oxide/propylene oxide, trimethylolpropane/propylene oxide, sucrose/propylene glycol/propylene oxide, 15 alkylamine/propylene oxide, and glycerine/propylene oxide, and mixtures thereof.

Also somewhat less preferred, the compositions of the present invention may optionally contain from about 0.01 - 50.0 percent by weight of an auxillary polyester polyol, i.e. a non-phthalic anhydride-based polyester polyol, such as for example, a polyester polyol derived from the condensation of caprolactone and a poly alcohol.

20 The polyisocyanate starting components used according to the present invention include aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic polyisocyanates, such as those described, for example, by W. Siefken in Justus Liebigs Annalen der Chemie 562: 75-136. Examples include ethylene diisocyanate; tetramethylene-1,4-diisocyanate, hexamethylene-1,6-diisocyanate; dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; 25 cyclohexane-1,3- and 1,4-diisocyanate and mixtures of these isomers; 1-isocyanato-3,3,5-

trimethyl-5-isocyanatomethylcyclohexane (German Auslegeschrift No. 1, 202,785, U.S. Pat. No. 3,401,190); hexahydrotolylene-2,4- and 2,6-diisocyanate and mixtures of these isomers; hexahydrophenylene-1,3- and/or -1,4-diisocyanate; perhydrodiphenylmethane-2,4'- and/or 4,4'-diisocyanate; phenylene-1,3- and -1,4-diisocyanate; tolulene-2,4- and -2,6-diisocyanate and mixtures of these isomers; diphenylmethane-2,4'- and/or -4,4'-diisocyanate; naphthylene-1,5-diisocyanate; triphenyl methane-4,4',4''-triisocyanate; polyphenyl-polymethylene polyisocyanate which may be obtained by aniline/formaldehyde condensation followed by phosgenation and which have been described, for example, in British Pat. Nos. 874,430 and 848,671; m-and p-isocyanatophenyl sulphonyl isocyanate according to U.S. Pat. No. 3,454,606; perchlorinated aryl polyisocyanate as described, for example, in U.S. Pat. No. 3,277,138; polyisocyanate; containing carbodiimide groups as described in U.S. Pat. No. 3,152,162; the diisocyanates described in U.S. Pat. No. 3,492,330; polyisocyanates containing allophanate groups as described, for example, in British Pat. No. 994,890, Belgian Pat. No. 761, 626 and Published Dutch Patent application No. 7,102, 524; polyisocyanates containing isocyanurate groups as described, for example, in U.S. Pat. No. 3,001,973, in German Pat. Nos. 1,022,789; 1,222,067 and 1,027,394 and in German Offenlegungsschriften Nos. 1,929,034 and 2,004,048; polyisocyanates containing urethane groups as described, for example, in Belgian Pat. No. 752,261 or in U.S. Pat. No. 3,394,164; polyisocyanates containing acrylated urea groups according to German Pat. No. 1,230,778; polyisocyanates containing biuret groups as described, for example, in U.S. Pat. Nos. 3,124,605 and 3,201,372; and in British Pat. No. 889,050; polyisocyanates prepared by telomerization reactions as described, for example in U.S. Pat. No. 3,654,016; polyisocyanates containing ester groups as mentioned, for example, in British Pat. Nos. 965,474 and 1,072,956, in U.S. Pat. No. 3, 567,763 and in German Pat. No. 1,231,688; reaction products of the above-mentioned isocyanates with acetals according to German Pat. No. 1,072,385; and,

polyisocyanates containing polymeric fatty acid groups as described in U.S. Pat. No. 3,455,883, and mixtures thereof.

The distillation residues obtained from the commercial production of isocyanates and which still contain isocyanate groups may also be used, optionally dissolved in one or more of the above-mentioned polyisocyanates.

Other suitable polyisocyanates which are readily available include, for example, toluene-2,4- and -2,6-diisocyanate and mixtures of these isomers ("TDI"); polyphenyl polymethylene polyisocyanates which may be obtained by aniline/formaldehyde condensation followed by phosgenation ("crude MDI"); and, polyisocyanates containing carbodiimide groups, urethane groups, allophanate groups, isocyanurate groups, urea groups or biuret groups ("modified polyisocyanates"), and mixtures thereof.

Somewhat more preferred polyisocyanates are 2,4- and/or 2,4/2,6-toluene diisocyanate, diphenyl methane 4,4'-diisocyanate, hexamethylene diisocyanate, and isophorone diisocyanate, and mixtures thereof.

Suitable polyisocyanurates useful in the present invention include, among others, as is well known to those skilled in the art the cyclotrimerization of any of the aforementioned polyisocyanates.

Compositions of the present invention may contain optional ingredients, including for example, rheology modifiers, plasticizers, pigments, and waxes.

The invention further encompasses urethanes suitable for use in a coating, adhesive, sealant and/or elastomer, wherein the urethane is made by polymerizing the inventive compositions described herein.

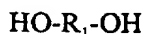
The present invention further encompasses a pre-urethane composition for preparing a urethane coating, adhesive, sealant and/or elastomer, comprising:

(a) from about 10 % to about 60% based on the weight of the composition of an isocyanate;

(b) from about 50% to about 90% based on the weight of the composition of a high aromatic, low acid number phthalate polyester polyol blend comprising:

5 (1) from about 20 - 60 weight percent of a phthalic acid material selected from the group consisting of phthalic anhydride or phthalic acid; and

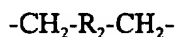
(2) from about 40 - 80 weight percent of at least one polyol of the formula:



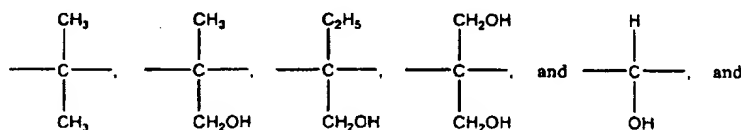
wherein R_1 is a divalent radical selected from the group consisting of:

10 (a) alkylene radicals of about 2 to 10 carbon atoms;

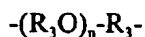
(b) radicals of the formula:



where R_2 is a radical selected from the group consisting of:



15 (c) radicals of the formula:



where R_3 is an alkylene radical containing from about 2 to about 4 carbon atoms, and n is an integer of from about 0.1 to 200.

20 Hydrolysis Studies

In general, hydrolysis of polyester polyols produces carboxylic acid moieties within a particular CASE composition, as shown below:



The formation of such carboxylic acid groups increases the acid number of the composition. Acid number is defined as the number of titratable -COOH groups present in a solution; the -COOH groups are titrated with dilute caustic, such as KOH.

Acid numbers (AN) are calculated using the equation

5

$$AN = (5.61)X(\text{ml of } 0.1 \text{ N Base})/\text{grams of polyol sample}$$

Sample sizes are generally 10 - 12 grams and the accuracy of the balance utilized is ± 0.01 gram. The standardized base is accurate to $\pm 0.0002 \text{ N}$; the limiting factor for accuracy of the equation is dominated by the titor volume. While the electronic burette used records milliliters of base to the nearest 0.001 ml, judgment in observing endpoints is the primary source of reproducibility variances. Experience suggests the latter effect is $\pm 0.1 \text{ ml}$; with a 10.00 gram sample and 1.5 ml of base titration, the relative error is about 0.06 AN, which is taken as the maximum relative error of any single acid number reported herein. Water levels (as % moisture) were determined per Stepan Test Method 022-0 with a Karl Fischer autotitrator.

As used in the Examples and description appearing below, the following designations, symbols, terms and abbreviations have the indicated meanings:

<u>Material</u>	<u>Description</u>
20 STEPANPOL® PS-2002	~200 OH # phthalic anhydride/diethylene glycol polyester; Acid Number = 0.64
TONE 0201	~200 OH # polycaprolactone glycol; Acid Number = 0.13
25 Adipic Acid Benzoic Acid Half-Acid Ester (HAE)	Reaction product from one mole each of phthalic acid and diethylene glycol
30 Desmodur N-3200	1,6-hexane diisocyanate trimer

Formrez® 11-225

~200 OH # diethylene glycol/adipic acid polyester glycol

"Liquid" MDI

methylene-diphenylene isocyanate

5

In the following examples, all amounts are stated in percent by weight of active material unless indicated otherwise. One skilled in the art will recognize that modifications may be made in the present invention without deviating from the spirit or scope of the invention. The invention is illustrated by the examples contained within; such examples are not to be construed as limiting the invention or scope of the specific procedures or compositions described herein.

The hydrolytic stability of StepanPol® PS-2002 and Fomrez® 11-225, with the addition of 2 weight percent water, was studied over several days. The 2 % aqueous polyester polyols were kept at 120° C and hydrolytic stability determined by monitoring changes in acid number. After 24 hours, titration of the two samples showed no detectable increase in the acid number of the STEPANPOL® PS-2002, whereas the aliphatic polyester showed a slight increase in acid number. After 100 hours of storage at 120° C, the STEPANPOL® PS-2002 exhibited an acid number which was approximately two times its original acid number, whereas the aliphatic polyester exhibited an acid number approximately 12 times its original acid number. From this experiment, STEPANPOL® PS-2002 is more hydrolytically stable than the diethylene glycol/adipic acid polyester glycol aliphatic analogue.

Without being bound by any particular theory, it is believed that the differences in susceptibility to hydrolysis between aromatic and aliphatic polyester polyols is based on resonance stabilization: The aromatic ring of an ortho phthalate ester, such as STEPANPOL® PS-2002, tends to distribute electrons over a benzene ring, making the adjacent carbonyl carbon less electropositive than an aliphatic carbonyl carbon analogue, and therefore the

carbonyl carbon in a aromatic polyester polyol possesses less affinity for a nucleophile, such as water.

Various polyester polyols, water and acid additives were combined to make the sample compositions designated in Table I. Adipic and benzoic acids are dissolved in warm polyol, and all other polyols were warmed (i.e. to about 90 - 100°C) prior to blending to provide uniform sample preparation.

Initial acid numbers are obtained within 30 minutes of each sample preparation. Sample jars are snugly fitted with foil-lined plastic caps and placed in a 200° F oven, with occasional removal and sampling for acid number evaluation. Water levels are occasionally determined for the samples by standard Karl Fischer titration; after 192 hours of aging at 200° F, the moisture level was found to be 2.01 wt.% for sample A, 1.93 wt.% for B, 2.16 wt.% for C and 9.48 wt.% for D. Because the hydrolysis of an ester group results in the formation of an organic acid, acid number measurement provides a convenient method for following the reaction of water with polyester polyols. Table II lists acid number results obtained from the samples in Table I which were exposed to 200° F for differing time intervals.

Hydrolysis of polyester polyols can be acid-catalyzed (see Kemp and Vellaccio, Organic Chemistry, Worth Publishers, 1980, p.372 and Lowry, Thomas H. et al. Mechanisms in Theory in Organic Chemistry, Second Ed., Harper and Row Publishers, N.Y., 1981, p. 658.) or base-catalyzed.

Table I
Sample Formulations

<u>Sample Designation</u>	<u>Polyester Polyol (g)</u>	<u>Water (g/wt.%)</u>	<u>Additives (g)</u>
A	PS-2002® (100g)	2g/2 wt.%	---
B	Tone® 0201 (100g)	2g/2 wt.%	---
C	Fomrez®11-225 (100g)	2g/2 wt.%	---

5	D	Fomrez® 11-225 (100g)	28g/22 wt. %	--
	E	Tone® 0201 (147g)	3g/2 wt. %	Adipic Acid (0.1088g)
	F	Tone® 0201 (147g)	3g/2 wt. %	Benzoic Acid (0.1836g)
	G	Tone® 0201 (147g)	3g/2 wt. %	HAE* (0.37g)
	I	PS-2002® (147g)	3g/2 wt. %	---
10	J	PS-2002® (150g)	17g/10 wt. %	---
	K	Tone® 0201 (150g)	17g/10 wt. %	
15	* HAE = Half Acid-Ester of phthalic anhydride and diethylene glycol			

Table II: Acid Number Results

20	Sample Designation	-----Hours of aging at 200° F-----							
		0	24	48	72	96	144	192	240 296
25	A (PS-2002®)	0.64	0.65	0.72	0.75	0.86	-	1.11	
	B (Tone®)	0.13	0.19	0.20	0.25	0.40	-	2.38	
	C (Fomrez®)	0.85	1.11	1.34	1.75	2.83	-	11.28	
	D (Fomrez®)	0.71	4.89	12.5	27.2	63.6	-	137.1	
	E (Tone®/Adipic)	0.71	0.87	-	1.20	-	2.08	-	
30	F (Tone®/Benzoic)	0.71	1.08	-	1.76	-	3.28	-	
	G (Tone®/HAE)	0.74	1.50	-	3.25	-	6.97	-	
	I (PS-2002®)	0.77	0.81	0.87	-	-	1.00	-	
	J (PS-2002®)	1.10	1.40	-	1.73	-	-	2.50 2.80	3.57
	K (Tone®)	0.12	0.44	-	0.40	-	-	2.60 4.81	17.8

Without being bound by any particular theory, it is believed that the apparent hydrolytic stability of Tone® polyester polyols over adipate based polyester polyols is a consequence of the inherently low acid number of polycaprolactone polyesters. Tone® polyesters are prepared by the glycol-initiated ring-opening of caprolactone, while adipate polyesters are the condensation products of glycols and adipic acid, wherein the condensation leaves residual acid if the reaction is not complete. Consequently, Tone® polyesters are more

hydrolytically stable than the corresponding adipate polyesters not from structure point of view, but rather from a deminished acid catalysis point of view.

As shown graphically in **Figure 1**, data reported for Samples E, F and G in **Table II** shows that Tone®0201 spiked with adipic acid, benzoic acid or the half acid ester of phthalic anhydride, causes an increase of the samples acid number over time at a rate similar to that of the Fomrez®11-225 samples C and D **Table II**.

Figure 3 shows samples K and L which support the concept that STEPANPOL® PS-2002 hydrolyzes more slowly than Tone®0201, as the ester linkages in the former are more sterically hindered and more difficult to hydrolyze than the latter.

Hydrolysis of STEPANPOL® PS-2002 produces a half acid-ester, the production of which would lead to a higher overall acid concentration. Increased acid concentration and strength favor an increase in the rate and the amount of hydrolysis of polyester polyols, and therefore one would expect to observe STEPANPOL® PS-2002 should exhibit a similar increase in acid number, as compared to the other polyester polyols tested. To evaluate the possibility that the ortho-substitution in STEPANPOL® PS-2002 impedes hydrolysis, studies with 10% water were conducted with PS-2002, a terephthalate based polyester polyol, and an isophthalate based polyester polyol, each of which contain diethylene glycol and have an OHv of 200. The increase in acid number, as shown in Figure 4, of the terephthalate and isophthalate based polyester polyols is greater than that for the STEPANPOL® PS-2002.

The observed order of decreasing stability against hydrolysis is STEPANPOL® PS-2002 > Tone®0201 >> Fomrez®11-225. The apparent hydrolytic stability of Tone®0201 over Fomrez®11-225 is the result of the windfall low acid content of the former compared with the latter. Furthermore, Tone®0201 which contains the same type and amount of acid as Fomrez®11-225 exhibits approximately the same rate of hydrolysis as the diethylene glycol

adipate polyester polyol. In general, without being bound by any particular theory, it is believed that a low acid number, a consequence of the manufacturing process, gives polycaprolactone polyols greater hydrolytic stability, as compared to the adipic and other aliphatic acid-based polyester polyols.

5 Carboxylic acids catalyze hydrolysis of the systems examined herein and most likely catalyze other systems which differ only by molecular weight. Increasing the acid concentration and strength (K_a) accelerates such hydrolysis reactions. Without being bound by any particular theory, it is believed that the catalytic activity (at equal concentrations) towards hydrolysis of polyester polyols is most likely: Aromatic acid with electron
10 withdrawing groups > Aromatic Acid > Aliphatic Acid with electron withdrawing groups > Aliphatic acid.

Although the reaction products of water and STEPANPOL® PS-2002 are an alcohol and an aromatic acid with an electron withdrawing group, this polyol contains neighboring and sterically hindered ester moieties which make the material more resistant to hydrolysis
15 than polycaprolactone based polyester polyols, even under enhanced acidic conditions. The ortho substitution in STEPANPOL® PS-2002 is therefore quite propitious for CASE applications where resistance to attack by water is required.

Formulated Coatings—Accelerated Aging Study

20 Thin films of polyurethane samples were prepared by reacting either STEPANPOL® PS-2002 or 560 MW polycaprolactone diol with 1,6-hexane diisocyanate trimer (N-3200) in the presence of dibutyltin dilaurate (DBTDL). Formulations were cast onto glass and allowed to cure overnight before evaluating. Films were prepared for tensile strength evaluations per ASTM D 883 (dog-bone specimens).

Tensile strengths were obtained for half of the samples from each formulation to give initial values. The remaining half of the samples were soaked in deionized water at 99° C for two weeks and then similarly evaluated for final tensile strength. **Table III** gives formulation specifics and tensile strength results.

5

Table IIIFormulated Coatings

Component	Coating 1 (parts by weight (pbw))	Coating 2 (parts by weight (pbw))
StepanPol® PS- 2002	97.23	
Caprolactone		88.05
N-3200 (HDI biuret)	66.36	66.36
(DBTDL Catalyst)	0.19	0.18
Final Film		
Thickness, in.	0.015	0.040
Tensile Strength, psi (initial)	537	240
Tensile Strength, psi (final)	278	145
Tensile Strength Retention, %	52	60

Retention of tensile strength is similar for the STEPANPOL® PS-2002 phthalic acid diethylene glycol and the polycaprolactone diol-based systems. This is significant since the latter is generally known as one of the most hydrolytically stable polyester systems currently available.

10

Formulated Adhesives

Adhesive tests were done using the following formulations shown below. The formulations shown, Adhesive 1 and Adhesive 2, are simple 2% NCO one-component

moisture cured PUR (Polyurethane Reactive) adhesives prepared by combining two different warm polyols (i.e. at a temperature of about 70°) with an excess of liquid MDI (i.e. the ratio of polyol to isocyanate is about 1:1.7). The formulated adhesive is applied to two pieces of wood at a thickness of 0.05 inch. After curing for 48 hours, the wood is cut up into 1 inch x 0.5 inch pieces and immersed into a water bath at 200°F for 72 hours. An Instron is used to measure the block strength of the adhesive before and after immersion.

	<u>Component</u>	<u>Adhesive 1</u>	<u>Adhesive 2 (Comparative)</u>
10	PA/DEG (~110 OHv)	72.0	-
	Caprolactone (~110 OHv)	-	69.0
15	"Liquid" MDI	28.0	31.0

Table IV shows the block strength of the adhesives before and after aging for 72 hours. As can be observed, the polycaprolactone adhesive lost virtually all block strength, whereas the DEG-PA adhesive retained a higher percentage of block strength, indicating superior hydrolytic stability of the DEG-PA adhesive.

Table IV. Block Strength of Adhesive 1 and Adhesive 2 Before and After 72 Hour Aging.

<u>Adhesive</u>	<u>Before Aging (psi)</u>	<u>After Aging (psi)</u>	<u>% Retention</u>
DEG-PA (I)	325	65	20
PolyCap(II)	268	5	1.9

Acid Number Comparison of StepanPol® PS-2002/Tone® Blends

Acid Number was determined for various mixtures of a phthalic acid diethylene glycol polyester polyol (StepanPol® PS-2002) and polycaprolactone after aging at 93°C for various lengths of time. The study was conducted at 93° C with 10% water using, for example, aqueous solutions of 100% STEPANPOL® PS-2002, 75% STEPANPOL® PS-2002 + 25% polycaprolactone, 50% STEPANPOL® PS-2002 + 50% polycaprolactone, etc. The results are shown below in Table V.

Table V

Test formulation	% PS-2002	<u>Acid Number</u>				
		0 hours	24 hours	72 hours	196 hours	240 hours
1	0	0.124	0.440	0.400	2.620	4.810
2	25	0.360	1.100	3.890	21.410	30.840
3	50	0.611	1.688	4.970	20.820	28.150
4	75	0.834	1.920	4.850	14.160	17.890
5	100	1.125	1.400	1.730	2.460	2.800

10

All documents, e.g., patents and journal articles, cited above or below are hereby incorporated by reference in their entirety.

From the foregoing, it will be appreciated that although specific embodiments of the invention have been described herein for purposes of illustration, various modifications may be made without deviating from the spirit or scope of the invention.

15

WHAT IS CLAIMED:

1. In a method for preparing a hydrolytically stable, non-foam, urethane coating, adhesive, sealant and/or elastomer, the improvement comprising the adding of an amount sufficient to impart hydrolytic stability to the non-foam urethane coating, adhesive, sealant
5 and/or elastomer of a phthalic anhydride-derived or phthalic acid-derived polyester polyol.

2. A composition for preparing a non-foam urethane coating, adhesive, sealant and/or elastomer, comprising:

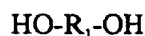
(a) from about 10 % to about 60% based on the weight of the composition of an
10 isocyanate;

(b) from about 0.02 % to about 5.0 % based on the weight of the composition of a urethane catalyst; and

(c) from about 50% to about 90% based on the weight of the composition of a high aromatic, low acid number phthalate polyester polyol blend comprising:

15 (1) from about 2 - 60 weight percent of a phthalic acid material selected from the group consisting of phthalic anhydride or phthalic acid; and

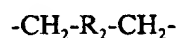
(2) from about 40 - 98 weight percent of at least one polyol of the formula:



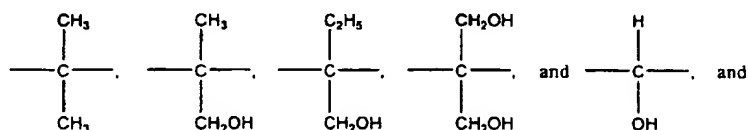
wherein R_1 is a divalent radical selected from the group consisting of:

20 (a) alkylene radicals of about 2 to 10 carbon atoms;

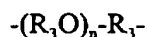
(b) radicals of the formula:



where R_2 is a radical selected from the group consisting of:



(c) radicals of the formula:



where R₁ is an alkylene radical containing from about 2 to about 4

5 carbon atoms, and n is an integer of from about 0.1 - 200; and

wherein the composition is substantially free of blowing agent.

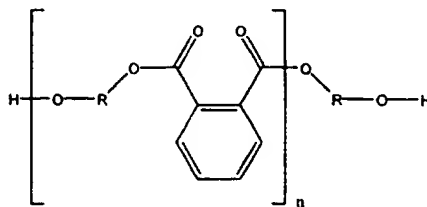
3. A composition according to claim 2, wherein the polyester polyol is a phthalic anhydride or phthalic acid diethylene glycol polyester polyol.

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4. A composition according to claim 2, wherein the isocyanate is 2,4- and/or 2,4/2,6-toluene diisocyanate, diphenyl methane 4,4'-diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, or mixtures thereof.

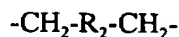
15 5. A composition according to claim 2, wherein the urethane catalyst is tetramethylbutanediamine (TMBDA), 1,4-diaza(2,2,2)bicyclooctane (DABCO), dibutyltin dilaurate (DBTDL) tin octoate (SnOct), or mixtures thereof.

6. A composition according to claim 2, wherein the polyester polyol is a
20 compound of the formula:

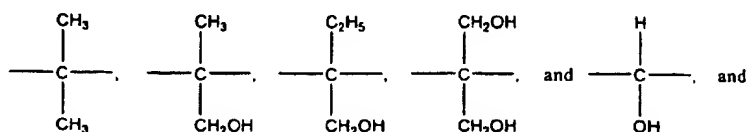


wherein R is a divalent radical selected from the group consisting of:

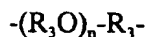
- (a) alkylene radicals of about 2 to 10 carbon atoms;
- (b) radicals of the formula:



5 where R_2 is a radical selected from the group consisting of:



- (c) radicals of the formula:



where R_3 is an alkylene radical containing from about 2 to about 4

10 carbon atoms, and n is an integer of from about 0.1 - 200; and

wherein n is 0.1 to 200.

7. A composition according to claim 2, additionally comprising from about 0.01 - 50.0 percent by weight of a polyether-based polyol.

15

8. A composition according to claim 2, additionally comprising from about 0.01 - 20.0 percent by weight of an auxillary polyester polyol.

9. A non-foam urethane suitable for use in a coating, adhesive, sealant and/or elastomer, the non-foam urethane made by polymerizing the composition of claim 2.

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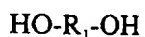
10. A pre-urethane composition for preparing a non-foam urethane coating, adhesive, sealant and/or elastomer, comprising:

(a) from about 10 % to about 60% based on the weight of the composition of an isocyanate;

(b) from about 50% to about 90% based on the weight of the composition of a high aromatic, low acid number phthalate polyester polyol blend comprising:

5 (1) from about 20 - 60 weight percent of a phthalic acid material selected from the group consisting of phthalic anhydride or phthalic acid; and

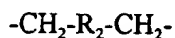
(2) from about 40 - 80 weight percent of at least one polyol of the formula:



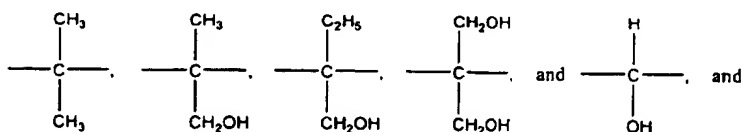
wherein R_1 is a divalent radical selected from the group consisting of:

10 (a) alkylene radicals of about 2 to 10 carbon atoms;

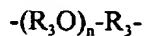
(b) radicals of the formula:



where R_2 is a radical selected from the group consisting of:



15 (c) radicals of the formula:

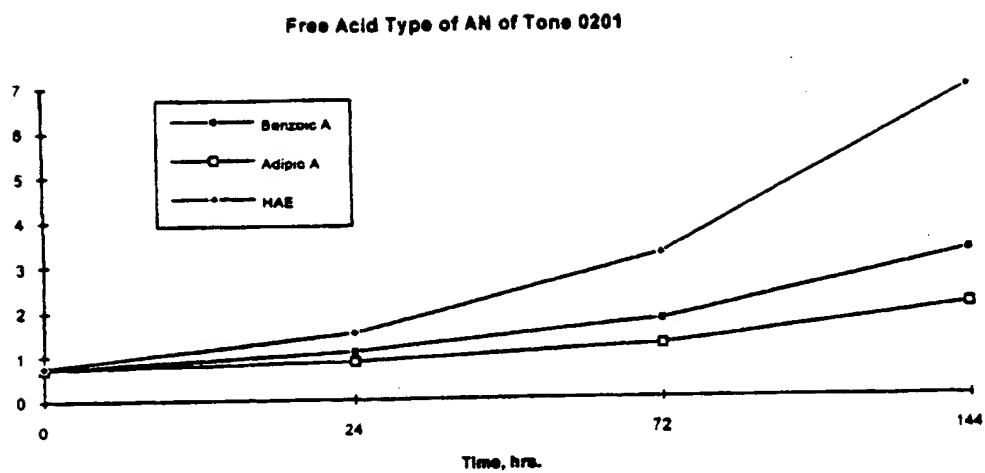


where R_3 is an alkylene radical containing from about 2 to about 4 carbon atoms, and n is an integer of from about 0.1 - 200;

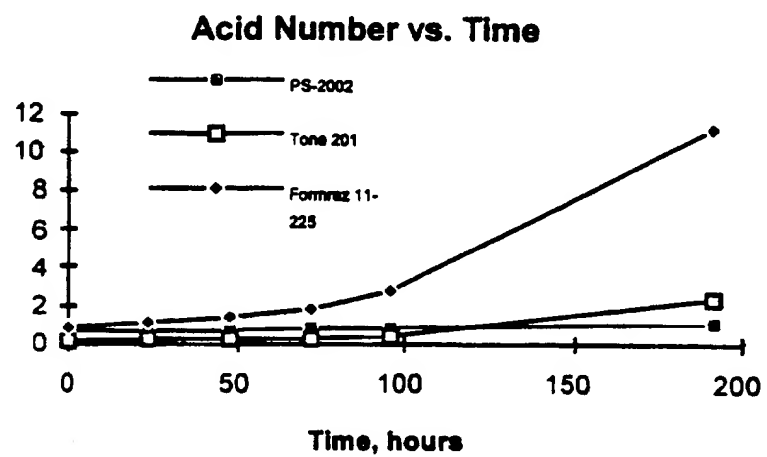
wherein the composition is substantially free of blowing agent.

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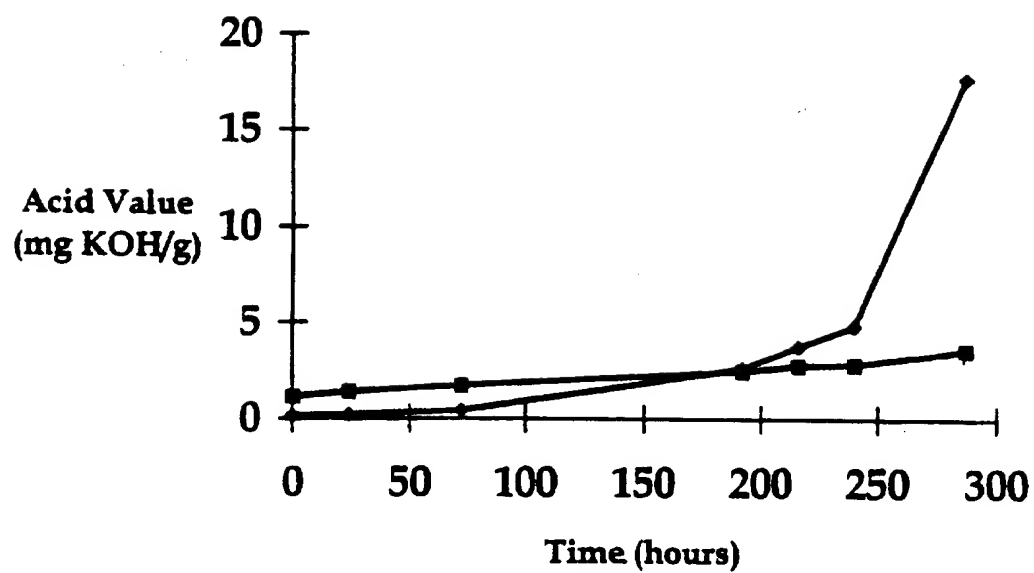
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Fig. 1

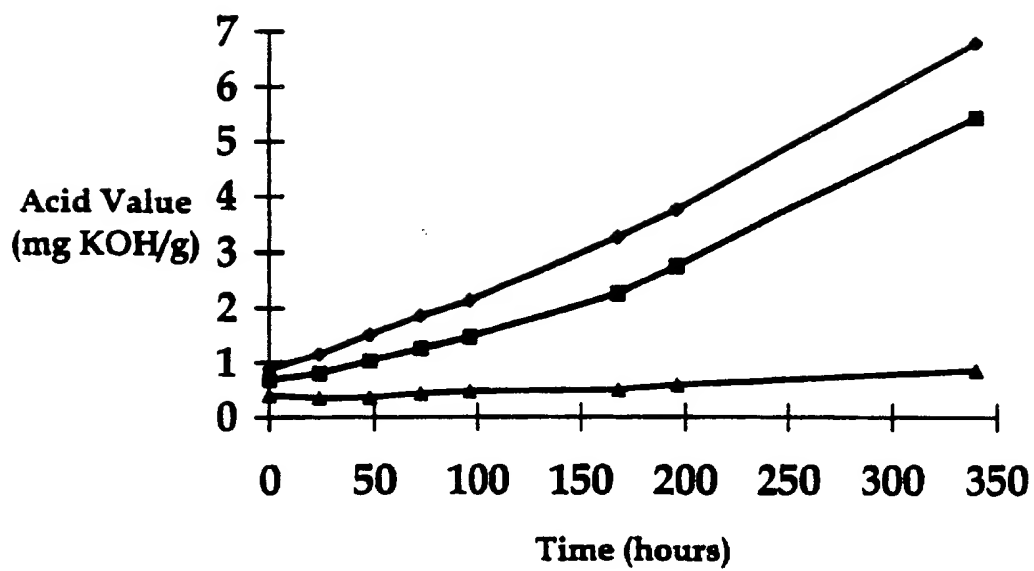
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Fig. 2

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Fig. 3

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Fig. 4

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 97/02113

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G18/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 143 304 A (BAYER AG) 5 June 1985 see page 3, line 11 - line 24; claims 1,2; examples 5,6	1-4,6,7, 9,10
A	US 4 038 256 A (A.F.FINELLI ET AL.) 26 July 1977 see claims 1,2; example 11	1-6,9,10
A	DE 20 61 957 A (LORENZ, OTTO) 6 July 1972 see page 2, line 9 - line 22; example 4	1-4,6
A	GB 2 248 844 A (NIPPON PAINT CO. LTD.) 22 April 1992 see claims 1,2,11-13	1-6,9,10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

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- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

3 June 1997

Date of mailing of the international search report

25.06.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Angiolini, D

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.
PCT/US 97/02113

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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